NATIONAL UNIVERSITY OF SINGAPORE

PC2230 Thermodynamics and Statistical Mechanics

(Semester II: AY2007-08, May)

Time Allowed: Two Hours

INSTRUCTIONS TO CANDIDATES

1. This examination paper contains **SIX SHORT** questions in Part I and **THREE LONG** questions in Part II. It comprises **TEN** printed pages.
2. Answer **ALL** questions in Part I. The answers to Part I are to be written on the question paper itself and submitted at the end of the examination.
3. Answer any **TWO** of the questions in Part II. The answers to Part II are to be written on the answer books.
4. This is a CLOSED BOOK examination. Students are allowed to bring in an A4-sized (both sides) sheet of notes.
5. The total mark for Part I is 48 and that for Part II is 52.

Matriculation No.	**Marks**

PART I

THIS PART OF THE EXAMINATION PAPER CONTAINS SIX (6) SHORT-ANSWER QUESTIONS FROM PAGE 2 TO 7.

Answer ALL questions. The answers are to be written on this question paper itself and submitted at the end of the examination.

1. An isolated gaseous system is partitioned by means of a movable diathermal wall into two subsystems.

   (i) Obtain the conditions for equilibrium.

   (ii) Show that when the two subsystems are not in pressure equilibrium, the subsystem at higher pressure expands and that at lower pressure contracts.

2. (i) Consider a system, initially at a temperature T_1, put in thermal contact with a heat bath at temperature T_0 $(T_1 < T_0)$. As the temperatures equalize, show that the entropy change of the system is given by $\Delta S = C \ln(T_0/T_1)$, where C is the heat capacity of the system.

(ii) One kilogram of water at $0^{\circ}C$ is brought into contact with a large heat reservoir at $100^{\circ}C$. When the water has reached $100^{\circ}C$, what has been the change in entropy of the water? Of the heat reservoir? Of the entire system consisting of both water and heat reservoir?

(Specific heat of water $= 4.2 Jg^{-1}K^{-1}$)

3. The Helmholtz free energy of a perfect classical gas of N molecules in an enclosure of volume V at temperature T is given by

$$F = -NkT \ln \left\{ \frac{eV}{N} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \right\} .$$

(i) Obtain an expression for the entropy of the gas.

(ii) The gas is allowed to expand freely into a vacuum so that it occupies a total volume of $2V$. Determine the change in entropy after equilibrium is established.

4. The Clausius-Clapeyron equation for the vapour pressure curve can be written as

$$\frac{dP}{dT} = \frac{L}{T\Delta V} ,$$

where L is the latent heat of vaporization.

(i) Assume the vapour is much less dense than the liquid and the vapour can be treated as an ideal gas. Show that

$$L = \frac{RT^2}{P}\frac{dP}{dT} .$$

(ii) Consider water vapour at $100^{\circ}C$ and $760 mmHg$. Experiments show that as the temperature increases from 99 to $101^{\circ}C$, the vapour pressure increases from 733.7 to $788.0 mmHg$. Determine $\frac{dP}{dT}$ and L.

$\left(R = 8.31\, Jmole^{-1}K^{-1}\right)$

5. The Fermi-Dirac energy distribution is given by

$$dN(\varepsilon) = \frac{4\pi V}{h^3}(2m)^{\frac{3}{2}}\varepsilon^{\frac{1}{2}}\frac{1}{e^{\beta(\varepsilon-\mu)}+1}d\varepsilon \ .$$

(i) At $T = 0K$, show that the Fermi energy is given by $\varepsilon_F = \frac{h^2}{2m}\left(\frac{3}{8\pi}\frac{N}{V}\right)^{\frac{2}{3}}$.

(ii) Define the Fermi temperature T_F and Fermi velocity V_F.

(iii) Given that the electron concentration is $4.7\times10^{22}cm^{-3}$, determine ε_F, T_F and V_F.

$\left(h = 6.626\times10^{-34}Js, \quad \text{electron mass} = 9.11\times10^{-28}\text{g}, \quad \text{k}=1.381\times10^{-23}\text{JK}^{-1}\right)$

6. The heat of reaction at constant volume Q_V and that at constant pressure Q_P for the chemical reaction $\sum_i \nu_i A_i = 0$ are related by $Q_V = Q_P - kT\sum_i \nu_i$ where Q_P is given by van't Hoff's equation

$$Q_p = kT^2 \frac{d}{dT} \ln K_p(T).$$

Show that $Q_V = kT^2 \frac{d}{dT} K_c(T)$, given the equilibrium constants for the reaction, $K_P(T) = \prod_i \left[kTf_i(T)\right]^{\nu_i}$ and $K_c(T) = \prod_i \left[f_i(T)\right]^{\nu_i}$.

PART II

THIS PART OF THE EXAMINATION PAPER CONTAINS THREE (3) LONG QUESTIONS AND COMPRISES THREE PAGES.

Answer any TWO questions.

1. A magnetic specimen of volume V consists of N dipoles, each having a magnetic moment of μ. In an applied magnetic field B, each dipole may orient itself parallel or antiparallel to B.

   (i) Show that the mean magnetic moment $\bar{\mu}$ and mean energy $\bar{E}$ of each dipole are given respectively by

   $$\bar{\mu} = \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial B}\right)_{\beta}, \qquad \bar{E} = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_{B},$$

   where Z is the partition function of one dipole.

   (ii) Show that the magnetization is given by

   $$I = \frac{N}{V}\mu \tanh x, \qquad x = \mu B \beta$$

   and hence derive the Curie's law.

   (iii) Show that $\beta = \frac{1}{2\mu B}\ln\frac{n}{N-n}$, where n is the number of dipoles oriented parallel to the field B. Show that the temperature can be negative. What happen when a system of negative temperature is allowed to exchange heat with that of positive temperature?

2. For a gas obeying the Maxwell speed distribution, the probability that a molecule should have a speed in the interval v to $v+dv$ is given by

$$P(v)dv = \frac{4}{\sqrt{\pi}}u^2 \exp(-u^2)du \text{, where } u \equiv v \Big/ \left(\frac{2kT}{m}\right)^{\frac{1}{2}}.$$

Show that the most probable speed $v_{\max}$, the mean speed $\bar{v}$ and the rms speed v_{rms} of the molecules are given respectively by

$$v_{\max} = \left(\frac{2kT}{m}\right)^{\frac{1}{2}}, \qquad \bar{v} = 2\left(\frac{2kT}{\pi m}\right)^{\frac{1}{2}}, \qquad v_{rms} = \left(\frac{3kT}{m}\right)^{\frac{1}{2}}.$$

Hence, show that the mean kinetic energy of the molecules $\bar{E} = \frac{3}{2}kT$.

$$\left(\int_0^\infty e^{-\alpha x^2} x^3 dx = \frac{1}{2}\alpha^{-2}, \qquad \int_0^\infty e^{-\alpha x^2} x^4 dx = \frac{3}{8}\sqrt{\pi}\alpha^{-\frac{5}{2}}\right)$$

3. The Bose-Einstein condensation of a perfect gas of bosons, each of mass m, in a cube of volume V is described by the following equation

$$N = \frac{1}{e^{-\beta\mu} - 1} + V\frac{2\pi(2m)^{\frac{3}{2}}}{h^3}\int_0^\infty \frac{\varepsilon^{\frac{1}{2}} d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1} .$$

(i) Describe how the gas exhibits a phase transition at a temperature T_c given by

$$T_c = \frac{1}{k}\left(\frac{N}{V}\right)^{\frac{2}{3}} \frac{h^2}{2\pi m}\left(\frac{1}{2.612}\right)^{\frac{2}{3}} .$$

(ii) Show how the number of bosons in the ground state varies as a function of temperature below T_c.

(iii) Derive the dependence of the heat capacity on temperature below T_c.

(iv) Compare the Bose-Einstein condensation with the ordinary vapour-liquid condensation.

$$\left(\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{z^{\frac{1}{2}}}{e^z - 1} dz = 2.612, \qquad \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{z^{\frac{3}{2}}}{e^z - 1} dz = 2.012 \right)$$

Ng S. C.

END OF PAPER